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(54) Title: POLYMERIC MULTILAYER HEAT EXCHANGERS CONTAINING A BARRIER LAYER (57) Abstract Heat exchangers which have heat exchange structures made from at least one layer of an organic polymer and at least one layer of a barrier polymer are particularly useful where light weight is important, such as in automobiles, trucks and aircraft.		

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POLYMERIC MULTILAYER HEAT EXCHANGERS CONTAINING A BARRIER
LAYER

FIELD OF THE INVENTION

5 This invention concerns a heat exchanger wherein the material which comprises the heat exchange surface structure contains at least one polymeric barrier layer and at least one polymeric thermoplastic layer.

TECHNICAL BACKGROUND

Heat exchangers are common pieces of equipment, used in many applications,
10 such as chemical processes, in automotive uses, household uses, and others. Heat exchangers are most commonly used to transfer heat between two fluids such as two liquids, a liquid and a gas, or between two gases. Traditionally, the materials used for the heat exchange surfaces are metals, which usually have relatively high thermal conductivities and good strength. However metals have certain drawbacks, such as high
15 forming and assembly costs, relatively high densities and therefore high weights, and sometimes poor corrosion resistance.

To overcome some of these disadvantages, heat exchangers using plastics have been developed. For instance, in highly corrosive environments heat exchangers using polytetrafluoroethylene (or perfluorinated tetrafluoroethylene copolymers) have been
20 used. However plastics have some inherent disadvantages, such as poorer heat transfer coefficients, in some cases relatively poor chemical stability, and permeability to the gas(es) or liquid(s) which contact the heat exchange surfaces. However, they often offer the advantages of lighter weight and easier fabrication than metals. Therefore, improved plastic heat exchangers are sought.

25 Japanese Patent Application 03/007891 describes a heat exchanger tube made from a liquid crystalline polymer and a filler having high heat conductivity. No mention is made of a tube having multiple layers of polymers.

French Patent Application 2,566,107 describes heat exchanger panels made from polymers such as polyethylene. No mention is made of layered plastics or barrier layers.

30 U.S. Patents 4,923,004, 4,955,435, 5,275,235 and 5,316,078 describe heat exchangers which employ various polyamides for the heat exchange surface materials. Barrier layers are not mentioned in these patents.

D. A. Reay, Heat Recovery Systems & CHP, vol. 9, p. 209-16 (1989), and I. H. Gross, Proceedings of Antec '93, p. 964-968 (1993) describe the use of polymers in heat exchangers. No mention is made of using layered polymer structures, nor of using LCPs.

SUMMARY OF THE INVENTION

This invention concerns, a multilayer heat exchanger containing a heat exchange surface material, said HESM comprising a polymeric barrier layer and a layer of a second polymer.

This invention also concerns a heat exchanger panel wherein a heat exchange surface material comprises a layer of a polymeric barrier layer and a layer of a second polymer.

By a heat exchange surface material (HESM) is meant a material which is used as part of a heat exchanger or a component thereof, and which is the material through which the major portion of the heat that is exchanged between the two fluids (gas or liquid) is meant to flow. It also performs the function of keeping the two fluids between which heat is being exchanged apart.

BRIEF DESCRIPTION OF THE DRAWINGS

Both figures 1 and 2 depict the apparatus that used to produce the film as described in Example 6.

Figure 1 is a schematic drawing from the side, of an apparatus for carrying out the multilayer film forming process described herein. An extruder, 1, supplies molten first thermoplastic to slit die 2 from which issues a molten multilayer thermoplastic film 3. A second extruder, 34, supplies molten second thermoplastic to slit die 2. A third extruder, 35, supplies molten third thermoplastic to slit die 2. The molten 3-layer film 3 falls vertically until it contacts approximately simultaneously embossed surfaces 7 and 8 of rollers 5 and 6, respectively. Rolling bank 4 of thermoplastic is also present. Rollers 5 and 6 are driven in rotation in the directions shown. Multilayer film 9 exits the gap from between rollers 5 and 6, goes between (optional) cooling rollers 9 and 10, and is wound up on windup roll 11.

Figure 2 shows the same rollers 5 and 6 and rolling bank 4 from the top, together with one method of oscillating the rollers 5 and 6 parallel to the axis (center line) of each of these rollers. Lever 9 is connected to a fixed point by pin 10, and to arms 13 and 14

by pins 19 and 20 respectively. The arms 13 and 14 are connected to rollers 5 and 6 respectively, through thrust bearings 15 and 16 respectively, allowing rollers 5 and 6 to rotate while being oscillated. Lever 9 contains slot 16 into which cam 17 is fitted.

Motor 18 rotates cam 17 thereby causing lever 9 to oscillate approximately

- 5 perpendicularly to the rotational axis of rollers 5 and 6. This causes 5 and 6 to oscillate in directions opposite to each other and parallel to their rotational axis.

In other words in this apparatus the molten multilayer film formed in the slit die 2 is passed through rollers which oscillate along the axis of rotation of the rollers, thereby imparting a transverse (to the direction of movement of the film) shearing action to the
10 molten polymer of the multilayer film.

DETAILS OF THE INVENTION

Heat exchangers described herein function to exchange heat (energy) between two fluids. These fluids may be gas(es) and/or liquid(s).

- One of the materials which is part of the HESM is a polymer layer (PL). By a
15 polymer layer is mean a layer that is made of a natural or synthetic polymer, preferably an organic polymer. It is also preferred that the PL is a thermoplastic. Any polymer may be used so long as it meets certain requirements. It must of course withstand the temperatures to which the HESM is exposed, and should throughout that temperature range provide sufficient strength (together with the barrier layer) to the HESM to
20 reasonably maintain its shape and contain the fluids in the heat exchanger, as needed, unless the HESM is deliberately designed to be flexible. If it is exposed to one or more of the fluids in the heat exchanger (or any other adventitious materials that may contact it) it preferably should be reasonably chemically stable to those fluids so as to maintain its integrity.

- 25 Although various types of heat exchangers made simply of single layers of polymers have been described, they sometimes have serious drawbacks when they are the only materials in HESMs. Sometimes the polymer of the HESM may not be chemically stable to one or more of the fluids in the heat exchanger, for instance, many polyesters hydrolyze or otherwise degrade in the presence of water, water-alcohol, or
30 water-glycol mixtures, especially at higher than ambient temperatures. Many polymers are relatively permeable to many liquids and/or gases, and therefore allow losses and/or migration of these materials in or from the heat exchanger. Some polymers may be

swollen by one or more of the fluids used in the heat exchanger thereby changing their dimensions and/or physical properties. All of the above are of course problems in polymeric heat exchangers.

5 It has been found that a polymeric barrier layer (PBL) used in the HESM often alleviates or eliminates one or more of the above mentioned problems. By a PBL is meant a layer whose polymer has a relatively low permeability to at least one of the fluids that are exchanging the heat energy. If a gas phase/liquid phase heat exchanger is being used, the permeabilities refer to the liquid phase.

10 The polymer of a PBL should have a permeability to a liquid or a gas which is 1/10 (0.10) or less, preferably about 1/100 (0.010) or less, than the permeability of the most permeable polymer layer in the multilayer structure. Alternatively the PBL should have a permeability to liquids of about 31 g-mil/m²/day (0.79 g-mm/m²/day) or less, preferably about 3.1 g-mil/m²/day (0.079 g-mm/m²/day) or less, or a permeability to gases (for a gas/gas heat exchanger) of about 100 ml-mil/m²/day (2.5 ml-mm/m²/day) or
15 less, preferably 10 ml-mil/m²/day (0.25 ml-mm/m²/day) or less. Permeability measurements on liquids to obtain these values should be at 38°C, while measurements on gases should be at 23°C.

If the PBL is placed between a fluid and any particular PL in the HESM it often protects that PL from chemical degradation by the fluid, and/or also often protects the PL
20 from being swollen by that fluid. For instance, in automotive heat exchangers which help cool the engine, the commonly used internal coolant is a mixture of a glycol and water, and the external coolant is air. With many PLs diffusion of water and/or glycol is so rapid that frequent replenishment of the water/glycol mixture is needed. If a PBL (to the water/glycol mixture) is included, the diffusion is greatly decreased.

25 Other barrier layer materials may also be used, for instance a metal in the form of a foil, a metalized surface or a ceramic in the form of a sputtered coating.

In order to obtain rapid heat transfer through the HESM, thickness through the material between the heat transfer fluids should be as small as possible. This would be true with any material used for an HESM, but is especially important with plastics since
30 their heat transfer coefficients are usually relatively low when compared to metals. Since the PBL is often the more expensive of the polymers present in the HESM, it is usually economically preferable to limit its use. Therefore, in most constructions it is preferred

that the PBL is present in relatively thin layer(s) and that layer(s) of the PL be relatively thick so as to carry much of the structural load of the HESM (i.e., pressure of the fluid(s), maintain structural shape and dimensions, etc.).

The HESM is made up of one or more PBL(s) and one or more PLs. If more than
5 PBL and/or PL is present, more than one type of PBL and/or PL, respectively, can be used. In addition other layers may be present. For example, so called tie layers (TL), also called adhesive layers, may be used to increase the adhesion between various PBLs and PLs, or between PLs or between PBLs. The number and placement of the various layers in the HESM will vary depending on the particular polymers chosen, the fluids
10 used in or by the heat exchanger, temperature requirements, environmental needs, etc.

Most commonly, tie layers and PBL(s) will be relatively thin compared to the PL(s). Typical constructions are given below, wherein Fluids 1 and 2 represent the fluids involved in the heat transfer:

- (a) Fluid 1/PBL/PL/Fluid 2
- 15 (b) Fluid 1/PL-1/PBL/PL-2/Fluid 2
- (c) Fluid 1/PBL-1/PL/PBL-2/Fluid 2
- (d) Fluid 1/PL-1/PBL-1/PL-2/PBL-2/Fluid 2
- (e) Fluid 1/PL-1/PL-2/PBL/Fluid 2
- (f) Fluid 1/PBL-1/PL-1/PL-2/PBL-2/Fluid 2

20 In all of the above constructions, tie layers may be present between all, some or none of the various polymer layers.

Some of the above constructions may be particularly useful in certain situations. If Fluid 1 but not Fluid 2 chemically attacked the PL, construction (a) may be particularly useful, but (c) and (f) may also be utilized. If both Fluids 1 and 2 attacked
25 the PL present construction (c) or (f) may be particularly useful. If one wanted to minimize diffusion of one fluid to another, a construction having two PBL layers, such as (c), (d) or (f) could be chosen. If a special surface is required to reduce abrasive damage on the Fluid 1 side, but great stiffness is also required from the PL, a construction such as (e) could be chosen wherein PL-1 and PL-2 have the requisite properties. These and
30 other combinations of layers having the correct properties for various applications will be apparent to the artisan.

Polymers useful as PBLs will depend on what the fluids that are being heat exchanged are. Permeabilities of various polymers are known or can be measured by known methods, see for instance ASTM E 96-95, ASTM F 1249-90 and ASTM D3985-95. These methods measure gas or vapor permeabilities, but may be readily modified to
5 measure the permeability of liquids, by using liquids in the measurement and having them contact the polymer whose permeability is being measured. When testing the permeability of a potential barrier polymer, it is preferred that test be carried out on a single layer of the barrier polymer itself. For a list of polymer permeabilities see S. Pauly in J. Brandrup, et al., Ed., Polymer Handbook, 3rd Edition, John Wiley & Sons,
10 New York, 1989, p. VI-435 to VI-449. If a polymer acts as a PBL in one particular heat exchanger, it may be only be a PL in another heat exchanger due to differing liquids in the two heat exchangers.

If one of the heat exchange fluids is a gas and the other is a liquid (during actual heat exchanger operation) it is preferred that the barrier layer be relatively impermeable
15 to the liquid. If both heat exchange fluids are liquids the barrier layer must be relatively impermeable to at least one fluid liquid, but is preferably relatively impermeable to both liquids. The same is true of a gas/gas heat exchanger. It is also preferred that the permeability of the barrier layer be measured under temperature conditions under which the heat exchanger typically operates.

20 One preferred heat exchanger herein is an automotive or other heat exchanger in which one fluid is water a water/alcohol mixture, or a water/glycol (such as ethylene glycol or 1,2-propylene glycol) mixture, and the other fluid is a gas, most commonly air. Here it is preferred that the barrier layer have a low permeability to the liquid fluid, the water, water/alcohol, or water/glycol mixture.

25 Polymers which may be useful in PBLs for liquids include various polyolefins such as polyethylene, polypropylene, ethylene/carbon monoxide copolymers and various polycycloolefins, fluoropolymers such as poly(tetrafluoroethylene), polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene 2,6-napthoate), other polymers such as poly(vinyl chloride), poly(vinylidene chloride), and
30 polyacrylonitrile. For use in PBLs for gases polymers such as fluoropolymers such as poly(tetrafluoroethylene), polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene 2,6-napthoate), polyamides such as nylon-6,6, nylon-6, and

high temperature nylons; and other polymers such as poly(vinyl chloride), poly(vinylidene chloride), polyacrylonitrile, copolymers of ethylene and vinyl alcohol, and poly(vinyl alcohol).

One preferred class of polymers for PBLs for both gases and liquids are liquid crystalline polymers (LCP). By an LCP is meant a polymer that is anisotropic when tested in the TOT Test described in U.S. Patent 4,118,372. These polymers tend to have very good barrier properties and are inert to many materials which are used as heat exchange fluids.

Useful LCPs include those described in U.S. Patents 3,991,013, 3,991,014 4,011,199, 4,048,148, 4,075,262, 4,083,829, 4,118,372, 4,122,070, 4,130,545, 4,153,779, 4,159,365, 4,161,470, 4,169,933, 4,184,996, 4,189,549, 4,219,461, 4,232,143, 4,232,144, 4,245,082, 4,256,624, 4,269,965, 4,272,625, 4,370,466, 4,383,105, 4,447,592, 4,522,974, 4,617,369, 4,664,972, 4,684,712, 4,727,129, 4,727,131, 4,728,714, 4,749,769, 4,762,907, 4,778,927, 4,816,555, 4,849,499, 4,851,496, 4,851,497, 4,857,626, 4,864,013, 4,868,278, 4,882,410, 4,923,947, 4,999,416, 5,015,721, 5,015,722, 5,025,082, 5,086,158, 5,102,935, 5,110,896, and 5,143,956, and European Patent Application 356,226. Useful thermotropic LCPs include polyesters, poly(ester-amides), poly(ester-imides), and polyazomethines. Especially useful are LCPs that are polyesters or poly(ester-amides). It is also preferred in these polyesters or poly(ester-amides) that at least about 50 percent, more preferably at least about 75 percent, of the bonds to ester or amide groups, i.e., the free bonds of $-C(O)O-$ and $-C(O)NR^1-$ wherein R^1 is hydrogen or hydrocarbyl, be to carbon atoms which are part of aromatic rings.

Included within the definition herein of a PBL is a blend of 2 or more polymers having the required permeability.

Useful thermoplastic polymers for PLs (or PBLs in the proper circumstances) are those that have the requisite properties as described above, and include: polyolefins such as polyethylene and polypropylene; polyesters such as poly(ethylene terephthalate, poly(butylene terephthalate), poly(ethylene 2,6-naphthalate), and a polyester from 2,2-bis(4-hydroxyphenyl)propane and a combination of isophthalic and terephthalic acids; styrenics such as polystyrene and copolymers of styrene with (meth)acrylic esters; acrylonitrile-butadiene-styrene thermoplastics; (meth)acrylic polymers including homo- and copolymers of the parent acids, and/or their esters and/or amides; polyacetals such as

polymethylene oxide; fully and partially fluoropolymers such as polytetrafluoroethylene, polychlorotrifluoroethylene, poly(tetrafluoroethylene/hexafluoropropylene) copolymers, poly[tetrafluoroethylene/perfluoro(propyl vinyl ether)] copolymers, poly(vinyl fluoride), poly(vinylidene fluoride), and poly(vinyl fluoride/ethylene) copolymers; ionomers such
5 as an ionomer of an ethylene-acrylic acid copolymer; polycarbonates; poly(amide-imides); poly(ester-carbonates); poly(imide-ethers); polymethylpentene; linear polyolefins such as polypropylene; poly(etherketoneketone); polyimides; poly(phenylene sulfide); polymers of cyclic olefins; poly(vinylidene chloride); polysulfones; poly(ether-sulfones); and polyamides such as nylon-6,6 nylon-6, nylon-6,12, nylon-6,12, nylon 4,6,
10 and the polyamides from terephthalic acid and 1,6-hexanediamine and/or 2-methyl-1,5-pentanediamine. Polyamides are preferred PLs and preferred amides are nylon-6,6, nylon-6, and a copolymer of terephthalic acid with 1,6-hexandiamine and 2-methyl-1,5-pentanediamine wherein 1,6-hexanediamine is about 30 to about 70 mole percent of the total diamine used to prepare the polymer. Especially preferred polyamides are nylon-
15 6,6, nylon-6 and a copolymer of terephthalic acid with 1,6-hexandiamine and 2-methyl-1,5-pentanediamine wherein 1,6-hexanediamine is about 50 mole percent of the total diamine used to prepare the polymer. Included within the definition of the polymer for a PL herein are blends of 2 or more polymers, for instance a polymer toughened with a rubber and optionally other ingredients.

20 Useful thermosetting polymers for PLs (or PBLs in the proper circumstances) are those that have the requisite properties as described above, and include epoxies, thermoset polyesters, and phenolics. These polymers will be formed into their final shapes before being crosslinked, as is normal with thermosetting polymers.

The polymers may contain other materials conventionally found in polymers,
25 such as fillers, reinforcing agents, antioxidants, antiozonants, dyes, pigments, etc. An especially useful material is a filler with high heat conductivity, which may increase the efficiency of the heat exchanger.

The composition of a tie layer will depend on which two polymers are on either side of it. For instance the tie layer may be the polymer of a PL functionalized or grafted
30 to provide adhesion between the PL and PBL layers, or may be a blend of one or more polymers of the PL and one or more of the polymers of the PBL(s).

Typical thicknesses for PL layers will range from about 0.025 to about 0.25 mm. Typical thicknesses for PBL layers will be about 0.01 to about 0.1 mm. Tie layers will usually be as thin as possible, consistent with their providing adhesion between polymer layers. This is usually about 0.01 to about 0.1 mm. The total thickness of the structure is
5 preferably less than about 0.7 mm, more preferably about 0.12 to about 0.5 mm, and especially preferably about 0.15 mm to about 0.4 mm.

Heat exchangers of many different configurations are, made and used, see for instance R. K. Shah, et al., in W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. B-3, VCH Verlagsgesellschaft mbH, Weinheim,
10 1988, p. 2-1 to 2-108. As can be seen from this article, and is well known in the art, probably the two most common heat exchange "elements" are the tube and the plate. In a tube type heat exchanger one of the fluids flow through a usually circular cross sectioned tube, while the other fluid flows on the exterior of the tube. Usually many small tubes are employed to create a large heat exchange surface. Sometimes the tubes
15 may be finned for more efficient heat transfer. In a plate element, small passageways, akin to small tubes, are fabricated within plate of the heat exchange material. One of the fluids flows on the inside of the passageways while the other fluid flows over the exterior surface of the plates. The passageways are usually small to increase surface area, and multiple plates are often used. All of the discussion about heat exchange surface
20 materials also applies to heat exchange panels.

For tube type heat exchangers containing LCPs, the multilayer material described herein can be made by multilayer coextrusion of a thermoplastic tube, see for instance U.S. Patent 5,288,529. However, LCPs when so extruded tend to be weak in the transverse direction (perpendicular to the long axis of the tube). Such problems can be
25 solved by using a counterrotating die for the LCP portion of the extruded tube, as described in U.S. Patents 4,963,428 and 4,966,807, and G.W. Farrell, et al., Journal of Polymer Engineering, vol. 6, p. 263-289 (1986). The tubes can be assembled into a full heat exchanger by inserting them into tanks with proper size holes and sealing the holes with a filler such as epoxy resin, or by heat sealing (e.g., melt welding).

30 Heat exchanger plates of the layered material described herein may be made by relatively standard methods. They may be directly coextruded, complete with passages in them. A flat sheet or film may be coextruded, thermoformed into the correct shape

and joined adhesively or by heat into the plate. Such coextrusions are known processes, see for instance H. Mar, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., Vol. 6, John Wiley & Sons, New York, 1986, p. 608-613, *ibid.*, Vol. 7, 1987, p. 106-127, all of which is hereby included by reference. Individual films or sheets of the PL(s) and PBL(s) may be laminated together, then formed into a heat exchanger plate. For fabrication of a plastic heat exchanger made with plates see U.S. Patent 4,955,435.

The heat exchangers described herein are useful for automotive and other vehicle uses, in aircraft, as comfort heat exchangers, and various ventilating, heating and air conditioning applications. They are particularly useful as liquid-gas heat exchangers used to cool automotive gasoline or diesel engines. In that case the liquid is usually water, water and a glycol, or water and an alcohol.

EXAMPLE 1

Small diameter tubing (~0.37 cm diameter and 250-310 μm wall thickness) was made with multilayer construction, nylon 66/LCP/nylon 66, using three extruders and a die to separately feed the different materials as separate layers. The LCP was a polyester of the composition 4,4'-biphenol/hydroquinone/terephthalic acid/2,6-naphthalene dicarboxylic acid/4-hydroxybenzoic acid/6-hydroxy-2-naphthoic acid (mole ratio 50/50/70/30/270/50). The LCP layer was about 51 μm thick. The tubing was sealed at one end, then filled with a 1:1 (vol.) mixture of commercial automotive antifreeze and water, subsequently sealed at the other end and then placed in an oven maintained at 100°C. The loss of the fluid with respect to time, was obtained by weighing. The loss was found to be : 0.5 gm/100 in² tubing surface area/day.

EXAMPLE 2

A heat exchanger was constructed from coextruded tubing (OD 0.366 cm, ID 0.328 cm) of configuration (inside of tube to outside) 64 μm HTN nylon/ 51 μm LCP (as in Example 1)/76 μm HTN nylon and active surface area of 1.959 m². The HTN was a blend of a polyamide which is a polymer of 1,6-hexanediamine and 2-methyl-1,5-pentanediamine (1:1 mole ratio) and terephthalic acid, with a synthetic rubber (Nordel® 3681, and EPDM-type rubber, available from E. I. DuPont de Nemours & Co., Wilmington, DE, 19898) and a functionalized synthetic rubber (which is a maleic anhydride functionalized EPDM) in an 85/15/5 weight ratio, respectively.

Hot water (81°C) was circulated through the exchanger while ambient air was passed across the surface of the tubes. Operation over a total of 24 days resulted in a loss of 201 gm water, equivalent to a water loss rate of 4.3 gm/m²/24 h.

EXAMPLE 3

5 A film of the following composition was produced by the blown film coextrusion method:

	layer 1	nylon 6/Sclair® 11K1 ^a /Fusabond® D226 ^b /a functionalized synthetic rubber ^c (72.5/13.6/6.8/6.8 weight percent)	0.05 mm
10	layer 2	XB603 (functionalized EMA)	0.01 mm
	layer 3	LCP	0.01 mm
	layer 4	XB603	0.01 mm
	layer 5	LCP	0.01 mm
	layer 6	XB603	0.01 mm
15	layer 7	Same as Layer 1	0.05 mm

^aLLDPE available from Nova Chemicals, Calgary, Alberta, Canada

^bA maleic anhydride grafted LLDPE available from E. I. duPont de Nemours & Co., Wilmington, DE U.S.A.

^cA maleic anhydride functionalized EPDM.

20

The LCP used was a polymer of the following monomers in the bracketed molar ratios; 4,4'-biphenol(26.3)/hydroquinone(26.3)/1,6-hexanediamine(47.4)/terephthalic acid(36.8)/2,6-naphthalene dicarboxylic acid(63.2)/4-hydroxybenzoic acid(89.5)/6-hydroxy-2-napthoic acid(36.8). Melting point (DSC) of this LCP was 265°C.

25 The film was used as a "lid" of an aluminum cup containing ethylene glycol: water mixture (a used ~1:1 ratio of commercial automotive antifreeze and water, radiator fluid), secured between metal rings and gaskets to avoid leakage and was placed in the inverted position (so that the liquid would contact the film) in an oven at 100 C. Periodically, the cup was removed from the oven, cooled and weighed and placed back in
30 the oven. The repeated cooling and reheating made the film concave or convex because of the pressure differences inside the cup as a consequence of the temperature variations.

This induces another repeated fatigue stress which can be qualitatively observed, but was not measured.

Evaluation of this film, at 60°C, showed a fluid loss of 0.81 gm/100 in²/day. A film (0.19 mm thick) of nylon-6,6 blended with synthetic rubber (Nordel® 3681) and
5 functionalized synthetic rubber (which is a maleic anhydride grafted EPDM) in an 80/10/10 weight ratio respectively (an also contains less than 1 weight percent of an epoxy resin), showed a loss of 10.27 gm/100 in²/day under the same conditions.

EXAMPLE 4

Tubing was extruded with the following configuration (inside to outside of tube)
10 and outer diameter 3.6 mm;

inside layer	LCP	0.05 mm
middle layer	XB603	0.05 mm
outer layer	nylon 6,6	0.075 mm

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The LCP used was a polymer of the following monomers in the bracketed molar ratios; 4,4'-biphenol(35.5)/hydroquinone(35.5)/1,6-hexanediamine(29.0)/terephthalic acid(60)/2,6-naphthalene dicarboxylic acid(40)/4-hydroxybenzoic acid(130). The melting point (DSC) of this LCP was 255°C.

20 Evaluation as per Example 1 at 38°C showed a loss of 0.02 gm/100 in²/day; nylon 6,6 tubing of the same dimensions showed a loss of 2.04 gm/100 in²/day.

Example 5

For this example a coextruded 3-layer film was used. When coextruded, the melt temperature of the inner layer was 269°C, while the melt temperature of the outer layers
25 was 292°C, and the line speed was 14.5 m/min. The inner layer, which was 0.076 mm thick, was Bynel® 4006 (this is a maleic anhydride modified high density polyethylene with a melt index of 0.6, available from E. I. DuPont de Nemours & Co., Wilmington, DE, U.S.A.) The two outer layers were the same polymer used for layer 1 of Example 3, and each outer layer was 0.057 mm thick. The film was corona treated on both sides to
30 about 48 dynes/cm.

The film was formed into heat exchanger panels consisting of 13 rectangularly shaped liquid flow channels with manifolds on each end, and each panel had a primary

heat exchange surface area about 54 cm long and 5 cm wide. Panels (67) were stacked by joining the manifolds, and the primary heat exchange surface of the stack was estimated to be 33,626 cm².

A similar heat exchanger was made from single layer film 0.19 mm thick of the same polymer of the outer layers of the above heat exchanger. This 69 panel heat exchanger had a surface area of about 34,632 cm².

Both of these heat exchangers were tested using 77°C water. The heat exchanger constructed from the 3-layer film had a water loss of 0.17 g/hr, while the heat exchanger constructed from the single layer film had a water loss of 1.1 g/hr.

10 Example 6

Polymer A was a liquid crystalline polymer which was an aromatic polyester, and was a copolymer of (molar ratios in parentheses): 4,4'-biphenol(26.3)/hydroquinone(26.3)/1,6-hexanediamine(47.4)/terephthalic acid(36.8)/2,6-naphthalene dicarboxylic acid(63.2)/4-hydroxybenzoic acid(89.5)/6-hydroxy-2-naphthoic acid(36.8).

Polymer B was a nylon 6/Sclair® 11K1^a/Fusabond® D226^b/a functionalized synthetic rubber^c (72.5/13.6/6.8/6.8 weight percent (^aLLDPE available from Nova Chemicals, Calgary, Alberta, Canada; ^bA maleic anhydride grafted LLDPE available from E. I. duPont de Nemours & Co., Wilmington, DE U.S.A.; ^cA maleic anhydride functionalized EPDM.)

Polymer C was a blend prepared in a twin screw extruder of 40 percent by weight of Polymer A and 60 percent by weight of Polymer B.

The apparatus used included a 3/4" (1.91 cm) Brabender (Type 2003, C. W. Brabender Instruments, Hackensack, NJ, U.S.A.), a 1" (2.54 cm) Wilmod extruder, and a 3.8 cm NRM extruder. Polymer A was extruded from the Wilmod extruder running at 45 rpm and the melt temperature was 280°C. Polymer B was extruded from the NRM extruder running at 20 rpm and at a melt temperature of 280°C. Polymer C was extruded from the Brabender extruder running at 60 rpm and with a melt temperature of 270°C. The output of each of these extruders was fed to 15.2 cm wide film die which was configured to handle three separate feeds. Polymers A and B were the outside layers and Polymer C was the inner layer.

The molten film fell by gravity on the oscillating rollers, which were arranged as shown in Fig. 1. The rollers were 8.9 cm in diameter and 20.3 cm wide, and the surfaces were faced with stainless steel which were embossed with a diamond or knurled pattern, about 50-75 μm deep, with a 90° included angle for the sides, with the knurling lines at an angle of 30° to the axis of rotation of the roll. The rotational speeds of the rollers were manually controlled using a variable speed drive motor and was set so the surface speed of the rolls was 6m/min. The rate of oscillation was also manually controlled by a variable speed drive motor and was 50 Hz, while the amplitude of oscillation could be varied by changing the cam 17, and was 1.3 mm. Each roller was individually heated by Calrod® electrical heaters, which were in turn automatically controlled by digital controllers. It is believed that the roller temperatures could be maintained to about $\pm 1^\circ\text{C}$, and the roller temperatures were 177°C. After passing through the oscillating rollers the film was passed through a set of cooling rolls and then rolled up on a roll.

In the beginning of the run, the speed of extrusion and rotation of the oscillating rollers were adjusted so that a rolling bank of the polymer built up on the oscillating rollers, and then the speed of the oscillating rollers was set as closely as possible to maintain a constant sized rolling bank. Occasionally some manual adjustments were needed.

In the resulting film, the Polymer A layer was about 0.051 mm thick, the Polymer B layer was about 0.10 mm thick and the Polymer C layer was about 0.051 mm thick.

Using the above three-layer film, heat exchanger panels were made using the procedure of Example 2 of U.S. Patent 5,050,671, as described below.

The sheets were coated on the Polymer B side with a solution of benzyl alcohol and phenol, as described in U.S. Patent 4,935,462. The coated sides were placed in face-to-face contact, between female molds containing grooves parallel to the long axis of the sheets, with inlet and outlet headers at each end of the sheets. The molds were then heated in a press at 160°C and 241 MPa pressure was applied while nitrogen gas was passed between the sheets so that each sheet conformed to the shape of the grooves, the two sheets were bonded together, and the headers were bonded to the ends of the sheets. No fractures or tears were evident in the resulting panel in the outer surfaces (which were Polymer A). The headers of several of these panels were bonded together to form a heat exchanger.

An otherwise identical heat exchanger was made from 0.2 mm thick sheeting of Polymer B (the sheeting didn't go through the oscillating rollers). Water at 70°C was passed through the two heat exchangers, and the rate of water loss by diffusion through the panels measured. The rate of water loss for the heat exchanger made with the three-
5 polymer layer panels was 0.8 g/hr more than 10 times less than that of the heat exchanger made from Polymer B alone which lost about 9.1 g/hr of water.

CLAIMS

What is claimed is:

1. A multilayer heat exchanger containing a heat exchange surface material, comprising, a polymeric barrier layer and a layer of a second polymer.
- 5 2. The heat exchanger as recited in claim 1 which is a liquid-liquid heat exchanger.
3. The heat exchanger as recited in claim 1 which is a liquid-gas heat exchanger.
4. The heat exchanger as recited in claim 1 which is a gas-gas heat exchanger.
5. The heat exchanger as recited in claim 1 which is used for automotive and
10 other vehicles, in aircraft, as a comfort heat exchanger, heating uses, air conditioning uses or for ventilating uses.
6. The heat exchanger as recited in claim 3 which is used to cool an automotive gasoline or diesel engine.
7. The heat exchanger as recited in claim 6 wherein said liquid is water, water and
15 a glycol, or water and an alcohol, and said gas is air.
8. The heat exchanger as recited in claim 1 which is a tube heat exchanger.
9. The heat exchanger as recited in claim 1 which is a plate heat exchanger.
10. The heat exchanger as recited in claim 1 wherein said polymeric barrier layer is a thermotropic liquid crystalline polymer.
- 20 11. The heat exchanger as recited in claim 10 wherein said thermotropic liquid crystalline polymer is an aromatic polyester or a poly(ester-amide).
12. The heat exchanger as recited in claim 1 wherein said second polymer is a polyamide.
13. The heat exchanger as recited in claim 6 or 7 wherein said second polymer is
25 a polyamide.
14. The heat exchanger as recited in claim 13 wherein said polymeric barrier layer is a thermotropic liquid crystalline polymer.
15. The heat exchanger as recited in claim 12 wherein said polyamide is nylon-6, nylon-6,6, or a copolymer of terephthalic acid, 1,6-diaminohexane and 2-methyl-1,5-
30 diaminopentane wherein said 1,6-diaminohexane is about 30 to about 70 mole percent of total diamine present.

16. The heat exchanger as recited in claim 13 wherein said polyamide is nylon-6, nylon-6,6, or a copolymer of terephthalic acid, 1,6-diaminohexane and 2-methyl-1,5-diaminopentane wherein said 1,6-diaminohexane is about 50 mole percent of total diamine present.

5 17. The heat exchanger as recited in claim 14 wherein said polyamide is nylon-6, nylon-6,6, or a copolymer of terephthalic acid, 1,6-diaminohexane and 2-methyl-1,5-diaminopentane wherein said 1,6-diaminohexane is about 30 to about 70 mole percent of the total diamine present.

10 18. The heat exchanger as recited in claim 1 wherein one or more tie layers are also present in said heat exchange surface material.

19. A heat exchanger panel wherein a heat exchange surface material comprises a layer of a polymeric barrier layer and a layer of a second polymer.

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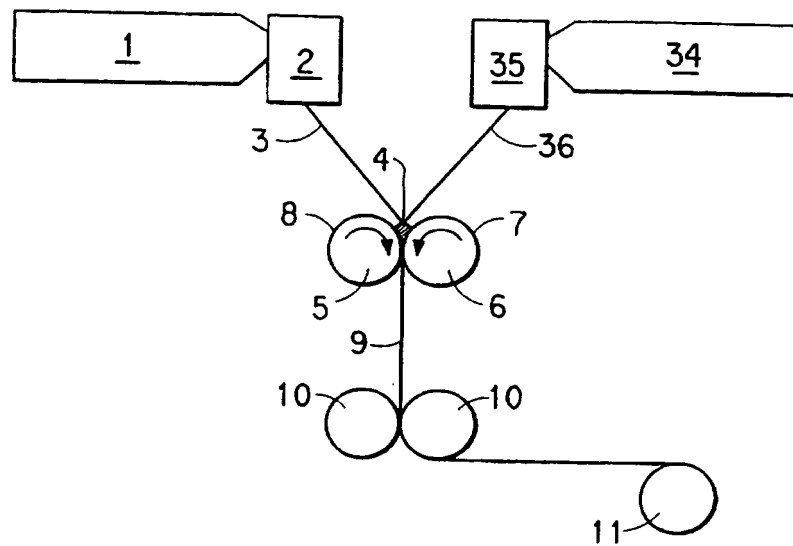


FIG. 1

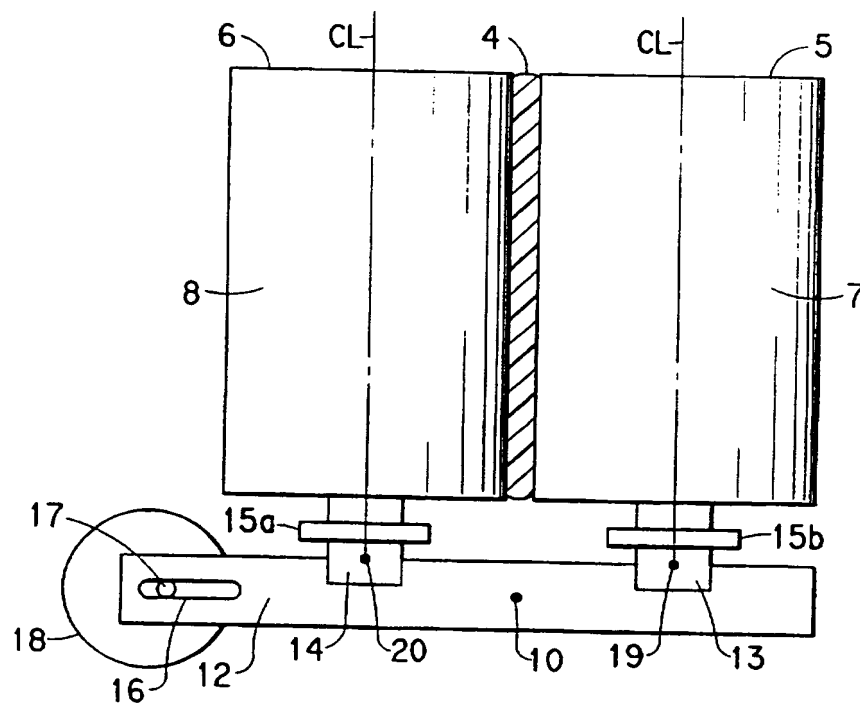


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No

PC1/CA 97/00647

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/08 F28F21/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B F28F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 485 671 A (LARSON RALPH I ET AL) 23 January 1996 see column 5, line 50 - column 6, line 47 ---	1, 5
X	WO 94 02257 A (BUCKLEY THERESA M) 3 February 1994 see claims 1, 7, 8 see page 5, line 19 - line 25 see page 7, line 14 - line 27 see page 17, line 8 - line 25 ---	1, 5, 10, 12
X	WO 96 03448 A (DU PONT) 8 February 1996 see claims 19-27 see page 9, line 9 - line 25 see page 16, line 19 - page 17, line 17 --- -/--	1, 5, 8, 12, 18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/CA 97/00647

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 340 520 A (SIEMENS AG) 8 November 1989 see claims 1-3; figures	1,5,9, 12,19
X	US 3 734 139 A (ZAFIROGLU D) 22 May 1973 see claim 1 see column 1, line 48 - column 2, line 14	1
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